A Rapid Method for the Determination of Gold and Silver in Sulfide Ores and Rocks

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A RAPID METHOD FOR THE DETERMINATION OF GOLD AND SILVER IN SULFIDE ORES AND ROCKS

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ABSTRACT

Gold and silver were determined in rocks and sulfide ores by flame and flameless atomic absorption spectrometry after decomposition of the samples with a mixture of aqua regia and bromine. Silver was determined directly by flame atomic absorption in the case of higher concentrations and with the graphite furnace for the low levels. Methyl isobutyl ketone was added to the remaining solution in order to extract and concentrate the gold which was determined by the graphite furnace procedure. Detection limits were 0.3 ng/g for gold and 10 ng/g for silver. The relative error, determined by analysis of standard rocks, was less than 5% for both elements. The precision was ±3.8% for gold at the 18 μg/g level and ±9.7% for silver at about the same concentration. About 50 samples a day can be analysed by this procedure.

RÉSUMÉ

Nous avons déterminé les teneurs en or et en argent dans des roches et des minerais par absorption atomique avec et sans flamme, après une décomposition des échantillons avec un mélange d'eau régale et de brome.

L'argent est déterminé directement par absorption atomique avec flamme pour les teneurs élevées et avec le four-graphite pour les basses teneurs. De la méthyl-isobutyl-cétone est ajoutée à la solution restante pour extraire et concentrer l'or, qui est déterminé par la technique du four-graphite. Les limites de détection sont de 0.3 ng/g (0.3 ppb) pour l'or et de 10 ng/g pour l'argent.

L'erreur relative (déterminée par l'analyse de roches-étalon) est inférieure à 5% pour les deux éléments. La précision est de ± 3.8% pour l'or au niveau de 18 μg/g et de ± 9.7% pour l'argent à une concentration à peu près équivalente. Il est possible d'analyser environ 50 échantillons par jour avec cette méthode.

ZUSAMMENFASSUNG

Gold und Silber werden nach einem Aufschluss der Proben in einer Mischung von Königswasser und Brom in Gesteinen und sulfidischen Erzen mit Atom-Absorptions-Spektrometrie bestimmt. Höhere Konzentrationen Silber wurden direkt mit Flammen-Atom-Absorption bestimmt, die niedrigen Werte mit dem Graphitrohrofen. Zu der verbleibenden Lösung wurde Methyl-iso-butylketon gegeben, um das Gold zu extrahieren und mit der Graphitrohrofen-Technik zu bestimmen. Die Nachweisgrenzen waren 0,3 ng/g (0,3 ppb) für Gold und 10 ng/g für Silber. Der relative Fehler (aufgrund der Analyse von Standard-gesteinen) war für beide Elemente kleiner als 5 %. Die Präzision war für Gold ± 3,8% (bei 18 μg/g) und für Silber ± 9,7 % bei etwa der gleichen Konzentration. Nach diesem Verfahren können etwa 50 Proben pro Tag analysiert werden.

INTRODUCTION

The geochemical laboratory is often faced with the need to determine gold and silver in large numbers of specimens of rocks and ores with a proper balance between accuracy and precision on the one hand and speed and cost of analysis on the other. A problem of some concern is that gold levels are very often below the detection limit of flame atomic absorption analysis, the preferred technique, even after use of the well-established procedure of concentration of gold by extraction into methyl isobutyl ketone (MIBK) where the detection limit is typically on the order of 1 μg/g in the original rock sample (1, 2). A further problem lies in the form of chemical attack used for the determination of silver. Hot aqua regia is often used to solubilize gold and it has often been assumed that such a procedure might precipitate silver as chloride ($K_{sp} = 1.8 \times 10^{-10}$) so that some workers use concentrated nitric acid (3) or a mixture of hydrofluoric, perchloric and nitric acids (4). In spite of the supposed risk of precipitating silver by use of aqua regia, this reagent is sometimes used (5) and a theoretical treatment shows that in fact silver is quite soluble in aqua regia because of the existence of chloro-complexes such as $AgCl_2^-$, $AgCl_3^{2-}$, $AgCl_4^{3-}$. From the known formation constants at zero ionic strength (6), it can be determined that the solubility of silver chloride is such as to give silver concentrations of 1.5 mg/L in distilled water, 8.1 mg/L in 1M hydrochloric acid, 130 mg/L in 3M acid, 900 mg/L in 6M acid and 4000 mg/L in 10M acid. The solubility of silver in a mixture of aqua regia and bromine is, however, unknown though it should be less than in aqua regia alone because of the lower solubility of silver bromide ($K_{sp} = 4.1 \times 10^{-13}$).

We have recently made a comparison of the nitric acid and aqua regia/bromine methods of decomposition of sulfide ores and rocks as a preliminary to the determination of silver and have demonstrated the limitations of the nitric acid attack. Use of aqua regia/bromine has the further advantage that gold may be determined in the same sample solution. We have developed a modification of existing procedures which is a simple, rapid and sensitive method for the determination of both elements in rocks, ores and minerals. The results of these investigations are presented here.

EXPERIMENTAL

Sample Preparation

Thirty-eight samples of sulfide ores and samples of auriferous rocks from Nova Scotia were used in this study. Original samples (> 1 kg) were broken into small pieces with the aid of a hammer and altered material was re-

moved by hand. The unaltered rock was pulverized to 100 mesh size in a ball mill then coned and quartered. Two further stages of grinding, coning and quartering were carried out until the mass of rock was reduced to about 100 g. This final sample was then ground to −200 mesh size. Because of the fine mesh size, it was possible to use small sample weights for analysis while still retaining good homogeneity of the analyte within the samples.

Sample Dissolution

Samples of ore or rock (0.5-1.0 g depending on the anticipated elemental content) were digested with 10 mL of aqua regia and a few drops of bromine. Heating was carried out until the volume was reduced to 5 mL. The digests were diluted to about 10 mL with distilled water and filtered into 20-mL polypropylene screw-top vials. Washing the residue gave a final volume of about 15 mL which was accurately recorded. An analogous series of decompositions was carried out with concentrated nitric acid only. The solubility of silver under these conditions was determined by adding 0.5 mL of saturated silver nitrate solution to 10 mL of aqua regia and repeating the procedure used for the ores.

Instrumentation

Higher concentrations of silver and gold (i.e., $>10\ \mu g/g$ in the solid sample) were determined directly in the solutions by flame atomic absorption analysis using a Jarrell-Ash Model 810 double-beam instrument with continuous background correction. Low concentrations of both elements were determined by flameless atomic absorption analysis using a Perkin-Elmer HGA-2200 graphite furnace coupled to a Varian-Techtron Model 475 double-beam atomic absorption instrument with continuous background correction. The absorption lines at 242.8 and 328.1 nm were used for gold and silver, respectively.

Selected ore samples were analyzed for silver using a neutron activation procedure. Samples were irradiated in a SLOWPOKE reactor with a flux of 5×10^{11} n $cm^{-2} s^{-1}$ for a period of 10 sec. After a decay time of 2 sec, counting was done for a 60-sec period and a second count was carried out 10 min after irradiation to make a correction for ^{76}As which interfered with the ^{110}Ag peak. A Tracor TN-1700 pulse height analyzer and Canberra Ge(Li) detector were used.

Procedure

After decomposition of ore and rock samples, gold and silver were determined by flame atomic absorption analysis whenever element concentrations were high enough. Silver was then determined in the remaining samples with the HGA, using 20-μL aliquots and the following program: drying stage, 125°C for 40 sec; charring stage, 400°C for 30 sec; atomization stage, 2700°C for 7 sec. Aliquots were diluted if necessary to reduce the final silver concentration to below 0.01 mg/L (0.2 ng in a 20-μL aliquot). Beer's law was not obeyed at higher silver concentrations.

After the determination of silver, the remaining volumes of solution were recorded accurately and were usually on the order of 12 mL. Where only the HGA procedure had been used, it was not necessary to remeasure the volume of solution because of the small sample volume used. To each sample 1 mL of MIBK was added and the vials were then capped and shaken for 5 min in a mechanical shaker. The organic layer was then analyzed for gold with the HGA, using 20-μL aliquots. Drying and atomization conditions were as for silver but the charring stage was 800°C for 30 sec. Standards with varying amounts of gold in 5 mL of 6M hydrochloric acid were diluted to 15 mL with distilled water and extracted into 1 mL of MIBK so that the solvent layer contained nominally 0.01, 0.005, 0.0025 and 0 mg/L gold. Actual concentrations were slightly higher because the solubility of MIBK in water is about 2%. Aliquots of the organic layer were diluted with more MIBK if gold concentrations exceeded 0.01 mg/L to keep values within the straight portion of the calibration curve. The calculated value for gold in the original sample made allowance for the loss of solution in the flame atomic absorption part of the procedure.

RESULTS AND DISCUSSION

Comparison of Sample Dissolution Procedures

The concentration of silver in the final solution, after addition of saturated silver nitrate to aqua regia and the same treatment used for the samples, was approximately 17 mg/L. If a conservative value of 15 mg/L is adopted, it is clear that for a dilution factor of 30 (i.e., 0.5 g sample diluted to 15 mL) silver concentrations not exceeding 450 $\mu g/g$ in the original ore or rock could be determined without risk of precipitation. In the present study, no silver values above 150 $\mu g/g$ were encountered.

Values obtained for aqua regia/bromine decomposition as a function of those obtained by nitric acid treatment are shown on logarithmic coordinates in Figure 1. Although at a first glance it might seem that the points are randomly distributed, a line through the 0.1-$\mu g/g$ coordinate with a slope of unity passes through or near (limits of broken lines) over half of the points. Such a line indicates a 1:1 relationship between the two sets of data. The most remarkable feature of Figure 1 is that of 16 points which are not close to or on the line, 13 are above the line, thus indicating that the aqua regia/bromine method of sample dissolution gives results for silver which are consistently higher than those obtained by nitric acid attack. The logarithmic coordinates (used to show all the points without crowding near the origin) in fact make the agreement between the data seem better than it really is. For example, a specimen of ore (#4) gave 70 $\mu g/g$ by aqua regia/bromine attack and only 2.5 $\mu g/g$ by nitric acid.

As a further check, silver was determined by neutron activation analysis (NAA) in 9 of the samples including some of the outliers. The data are shown in Table I which also contains values obtained by the two rock decomposition procedures. It is evident that in 7 of the samples, the aqua regia/bromine method of attack gave results closer to those obtained by the nondestructive NAA technique. In the more extreme cases such as sample #4, the NAA value was 72 $\mu g/g$ compared with 70 $\mu g/g$ for aqua regia and 2.5 $\mu g/g$ for nitric acid. A similar pattern was found in samples 17 and 33. These three specimens all contained sphalerite and galena as the major constituents.

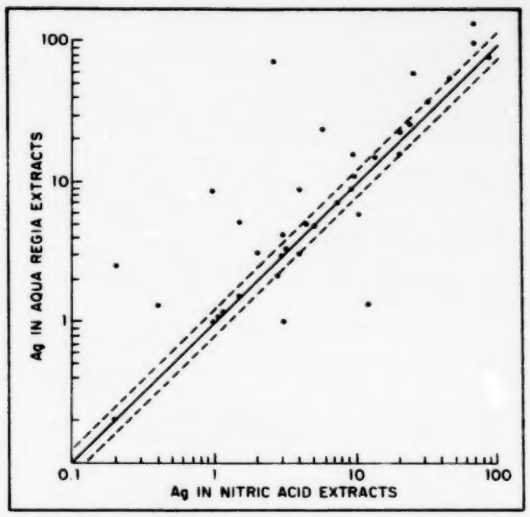

Fig. 1. Silver concentrations (μg/g) in sulfide ores analyzed by atomic absorption spectrophotometry after sample decomposition by aqua regia/bromine and by nitric acid.

It is concluded that the above data have clearly shown the deficiencies of the nitric acid method of attack compared with that involving aqua regia/bromine. The discrepancy between the two procedures seems to become greater as the silver concentration increases.

Gold and Silver Concentrations in Standards, Sulfide Ores and Rocks

Gold and silver concentrations in minerals, rocks and standards are shown in Table II. Only a few typical values are given since all ore values for silver concentrations have been shown in Figure 1. It will be noted that the data for the standard rocks are very close to recommended concentrations (7) and show that extraction of gold and silver is virtually quantitative with the aqua regia/bromine method of rock decomposition.

Detection Limits, Precision, Accuracy and Speed of Analysis

The data on standard rocks in Table II indicate a relative error of < 5% for both gold and silver determinations.

The precision as determined by 10 separate analyses of standard rocks (i.e., 10 separate rock decompositions) was ±3.8% for gold in MA-1 (17.8 μg/g) and ±9.7% for silver in the same sample (16.5 μg/g).

TABLE I
Comparison of Silver Concentration (μg/g) in Sulfide Ores Determined by Three Different Analytical Procedures

	Sample no.								
Procedure	*4*	*5*	*10*	*11*	*12*	*13*	*17*	*24*	*33*
Neutron activation analysis	72	99	16	5	15	16	150	9	120
A.A. after nitric acid attack	2.5	85	10	4.4	10	10	65	7.3	69
A.A. after aqua regia attack	70	78	15	5	6	11	125	7.5	100

TABLE II
Gold and Silver Concentrations (μg/g) in Rocks, Sulfide Ores and Standards

		Gold		*Silver*	
Sample	*Nature of sample*	*Rec.*	*Found*	*Rec.*	*Found*
KC-1*	Zn-Pb-Sn-Ag ore			1120	1150
MA-1*	Gold Ore	17.8	16.6		16.5
MP-1*	Zn-Sn-Cu-Pb ore			57.9	59.4
PTC-1*	Sulfide concentrate	0.65	0.67	5.80	6.04
5	Sulfide with arsenopyrite/pyrite		140		78
37	Sulfide with stibnite/quartz		16		16
9	Sulfide with sphalerite/galena		0.55		2
F-130	Auriferous rock		0.0073		n.d.
F-104	Auriferous rock		0.0021		n.d.
F-57	Auriferous rock		0.00084		n.d.
F-63	Auriferous rock		<0.00030		n.d.
AV-363	Granite		<0.00030		0.80
LL-10	Granite		<0.00030		0.08
KI-102	Granite		<0.00030		0.01

*Recommended value from Steger (7).
n.d. = not determined.

The detection limit was lower for gold than for silver because of the enrichment factor inherent in extracting all the gold into a small volume of MIBK. Limits of detection were therefore 0.0003 μg/g for gold and 0.01 μg/g for silver. These values refer to the original solid sample.

In a normal working day it is possible for one person to determine gold and silver in 50 samples without appreciable sacrifice of precision or accuracy.

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